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Vapor Pressures of Liquid Nitrogen Between the Triple and Critical Points

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Vapor pressure measurements available in the literature for liquid nitrogen between the triple point (T_t = 63.14° K., P_t = 94.01 mm.) and the critical point (T_c = 126.15° K., P_c = 33.52 atm.) have been comprehensively analyzed and used to evaluate the constants of the Frost-Kalkwarf equation. This equation for nitrogen was as follows:

$$\log P = 13.84475 - \frac{401.055}{T} - 3.06762 \log T + 0.11443\, P/T^2$$

where P is the vapor pressure in millimeters of Hg and T is the corresponding temperature in degrees Kelvin. This equation reproduced 180 experimental vapor pressure measurements over the complete liquid range with an over-all average deviation of 0.82%. This relationship has also been used to evaluate vapor pressures at convenient temperatures ranging from the triple point to the critical point of nitrogen.

A NUMBER of vapor pressure measurements of nitrogen have been presented in the literature since the turn of the century and extend over the range included between the triple and the critical points. The early vapor pressure measurements of Olzewski (*17*) in 1884 and those of Wroblewski (*24*) in 1886 represent an initial attempt to establish this property for liquid nitrogen at a time when cryogenic experimental techniques were not as well advanced to permit the establishment of reliable values. Despite these limitations, Olzewski (*17*) and Wroblewski (24) reported critical values for nitrogen. In addition, Sarrau (*20*) in 1882, and Dewar (*6*) in 1884 also presented critical values for this substance. The critical values reported by these investigators are as follows:

Year	t_c, ° C.	P_c, Atm.	
1882	−123.8	42.1	Sarrau (*20*)
1884	−146.0	35.0	Olzewski (*17*)
1884	−146.0	35.0	Dewar (*6*)
1885	−146.0	33.0	Wroblewski (*24*)

Although improved vapor pressure determinations continued to be made (*1, 8, 21*), it was not until 1914 when Kamerlingh Onnes, Dorsman, and Holst (*14*) carried out exacting measurements for nitrogen which included the critical point. They reported t_c = −147.13° C. or T_c = 125.96° K. based on a temperature scale of 273.09° K. and a critical pressure, P_c = 33.49 atm. Their critical temperature, adjusted to the present temperature scale of 273.16° K. based on the triple point of water, becomes T_c = 126.03° K. In 1915 Cardoso (*3*) reported for nitrogen t_c = −144.7° C. and P_c = 33.65 atm. Further attempts to establish these critical constants were not made until 1951 when White, Friedman, and Johnston (*23*) reported the results of their studies as T_c = 126.26±0.04° K. and P_c = 33.54±0.02 atm. The critical values reported recently by White, Friedman, and Johnston (*23*) and those reported earlier by Kamerlingh Onnes, Dorsman, and Holst (*14*) are in good agreement, and consequently, their average values, T_c = 126.15° K. and P_c = 33.52 atm., have been accepted in this study to represent the critical values of nitrogen. These values, along with the critical density, d_c = 0.3110 grams per cc. reported by Mathias, Kamerlingh Onnes, and Crommelin (*16*) produce for nitrogen a critical compressibility factor, z_c = 0.2918.

ANALYSIS OF VAPOR PRESSURE MEASUREMENTS

A comprehensive literature search indicated that the basic vapor pressure measurements, from the triple point to the critical point of nitrogen, were reported in 14 references as indicated in Table II. The experimental information of these references was used to develop the relationship of the reduced quantities log P_R *vs.* $1/T_R$ presented in Figure 1, which covers the range included between the triple point and the critical point. The relationship of Figure 1 permits the direct establishment of approximate vapor pressures, which can be improved if calculated with a more exact analytical expression.

The vapor pressure function of Frost and Kalkwarf (*10*) was derived from the Clapeyron equation based on the assumptions that, the volume of the liquid phase is negligible, the molar heat of vaporization is a linear function of absolute temperature, and the deviation of the vapor from ideal behavior can be represented by the introduction of the van der Waals' term, a/v^2. The expression derived from these assumptions has been shown to represent accurately the vapor pressure behavior of a number of substances (*2*, *19*, *21*), including the light hydrocarbons. Therefore, this relationship has been adopted in this study to analyze comprehensively the vapor pressure data of liquid nitrogen. The Frost-Kalkwarf vapor pressure equation

$$\log P = A + \frac{B}{T} + C \log T + D\frac{P}{T^2} \tag{1}$$

requires the establishment of four constants to represent properly the complete vapor pressure function between the triple point and the critical point of a substance. Its development showed (*10*) that $D = a/2.303R^2$ where a represents the van der Waals' constant and R is the gas constant. Since, $a = 27R^2T_c^2/64P_c$, then

$$D = \frac{27}{2.303(64)}\,\frac{T_c^2}{P_c} \tag{2}$$

where T_c and P_c represent the corresponding critical values. Thus, the value of D for nitrogen becomes

$$D = \frac{27(126.15)(126.15)}{2.303(64)(33.52 \times 760)} = 0.11443\ (^\circ\text{K.})^2/\text{mm.}$$

To obtain an accurate representation of constants A, B, and C, the adoption of an analysis that has the capability to screen out questionable data and at the same time permit the establishment of these constants from the reliable vapor pressure measurements is necessary.

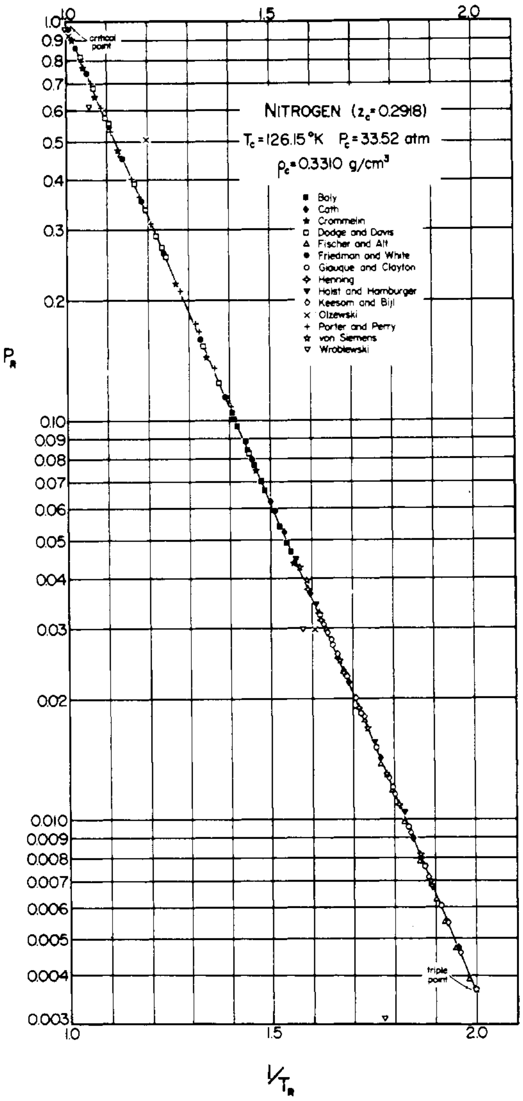

Figure 1. Vapor pressure relationship between log P_R and $1/T_R$ for liquid nitrogen

ESTABLISHMENT OF CONSTANTS A, B, AND C

With $D = 0.11443(^\circ\text{K.})^2$ per mm., Equation 1 can be rearranged as follows:

$$\log P - D\frac{P}{T^2} = A + \frac{B}{T} + C \log T \tag{3}$$

where the quantity $\log P - DP/T^2$ can be represented numerically for each experimental vapor pressure measurement. Thus Equation 3 represents a relationship that is linear in A, B, and C. Although a statistical analysis involving the method of least-squares could be adopted for the establishment of these constants using all of the available vapor pressure measurements, this approach was not used in favor of a method that possesses the capability of visually screening out data of a questionable nature. When Equation 3 is applied to a reliable reference point, (P_1, T_1), the following expression results:

$$\log P_1 - D\frac{P_1}{T_1^2} = A + \frac{B}{T_1} + C \log T_1 \tag{4}$$

Upon subtracting Equation 4 from Equation 3 constant A is eliminated, producing an equation of the form

$$\log\frac{P}{P_1} - D\left[\frac{P}{T^2} - \frac{P_1}{T_1^2}\right] = B\left[\frac{1}{T} - \frac{1}{T_1}\right] + C\log\frac{T}{T_1} \tag{5}$$

Equation 5 can be rearranged to produce the expression

$$\frac{\log\dfrac{P}{P_1} - D\left[\dfrac{P}{T^2} - \dfrac{P_1}{T_1^2}\right]}{\log\dfrac{T}{T_1}} = B\,\frac{\dfrac{1}{T} - \dfrac{1}{T_1}}{\log\dfrac{T}{T_1}} + C \tag{6}$$

To maintain consistency within a set of vapor pressure data, a reference point was selected from these values by plotting them as log P *vs.* $1/T$. An arbitrary experimental value, which fitted exactly the resulting relationship, was chosen as the reference point of the set. Using this selected reference point, the vapor pressure modulus, $Y = \{\log P/P_1 - D[P/T^2 - P_1/T_1^2]\}/\log T/T_1$, and the temperature modulus, $X = [1/T - 1/T_1]/\log T/T_1$, were calculated for each vapor pressure measurement with the aid of a CDC-3400 digital computer. As an example, the vapor pressure data of Friedman and White (*9*) and the resulting moduli Y and X using a reference point, T_1 = 102.02° K. and P_1 = 6697.6 mm., are presented in Table I. This procedure was applied to each of the 14 available sets of vapor pressure values and the resulting moduli Y and X are plotted as shown in Figure 2. The measurements of Cath (*4*), Crommelin (*5*), Dodge and Davis (*7*), Friedman and White (*9*), Giauque and Clayton (*11*), Henning (*12*), Keesom and Bijl (*15*), and Porter and Perry (*18*) produce Y and X values, which plot as straight lines in the range included between the triple point and the critical point. The best straight line drawn through the Y-X values has a slope of $B = -401.055$ and an intercept of $C = -3.06762$.

To define completely the vapor pressure behavior of nitrogen using Equation 1, A must now be determined. This was accomplished by selecting 95 of the experimental values used to generate the linear relationship of Figure 2. When these values were substituted into Equation 1 an average value of $A = 13.84475$ was obtained. As a result of this treatment, the vapor pressure behavior of liquid nitrogen becomes

$$\log P = 13.84475 - \frac{401.055}{T} - 3.06762 \log T + 0.11443 \frac{P}{T_2} \quad (7)$$

Equation 7 is applicable in the range included between the triple point (T_t = 63.14° K., P_t = 94.01 mm.) and the critical point (T_c = 126.15° K., P_c = 33.52 atm.). The experimental vapor pressures of each investigator were compared with values calculated using Equation 7 to produce the average deviations presented in Table II. The excessively high deviation of 116% encountered with the early data of Wroblewski (*24*) justifies their elimination from further consideration. Of the remaining 13 references, the vapor pressure values of Baly (*1*), Crommelin (*5*), Fischer and Alt (*8*), Holst and Hamburger (*13*), Olzewski (*17*), and Porter and Perry (*18*) produced deviations of more than 1% but not exceeding 2.04% encountered with the measurements of Fischer and Alt (*8*).

Equation 7 produces in the low pressure region, values which compare very favorably with the measurements of Giauque and Clayton (*11*) and Keesom and Bijl (*15*), giving rise to an average deviation in each case of 0.13%. In the high pressure region, Equation 7 yields values which produce an average deviation of 0.36% when compared with the corresponding measurements of Friedman and White (*9*).

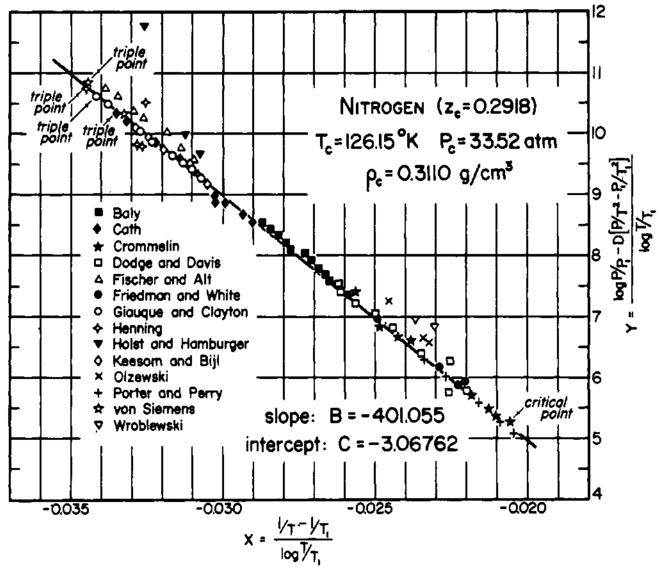

Figure 2. Linear relationship of Y vs. X for liquid nitrogen

To present vapor pressures for nitrogen over the complete liquid range, values were calculated using Equation 7 at convenient temperatures between T_t = 63.14° K. and T_c = 126.15° K. These calculated values are presented in Table III and represent the best compromise of the better experimental vapor pressure measurements presented in the literature. With the exclusion of the data of Wroblewski (*24*), which were reported in 1886 and produced extremely high deviations, 180 vapor pressure measurements were selected randomly from the remaining references. These vapor pressures were compared with values calculated using Equation 7 to produce an average deviation of 0.82%. The values used for this comparison include the efforts of a number of investigators who carried out these measurements as far back as the turn of the century and possibly lack the precision capable with modern techniques. The calculated triple point pressure P_t = 93.97 mm. compares very closely with the experimental value of Giauque and Clayton (*11*), P_t = 94.01 mm. The normal boiling point, T_b = 77.334° K., yields a vapor pressure of 759.4 mm. instead of 760.0 mm. The calculated critical pressure, P_c = 33.24 atm. gives rise to a deviation of 0.82% when compared with the averaged value of Kamerlingh Onnes, Dorsman,

Table I. Moduli Y and X Calculated from the Vapor Pressure Data of Friedman and White (9) for Nitrogen

T, ° K.	P, Mm.	Y	X
77.86	800.05	7.3636	−0.02591
83.66	1502.5	6.9636	−0.02496
86.85	2033.0	6.7937	−0.02449
90.90	2910.0	6.5579	−0.02392
95.05	4066.5	6.3309	−0.02339
98.96	5423.1	6.1550	−0.02292
102.02	6697.6	...	...
104.55	7898.7	5.8826	−0.02230
106.71	9106.3	5.9195	−0.02207
109.09	10436	5.7017	−0.02183
110.85	11556	5.6282	−0.02166
114.16	13897	5.5011	−0.02135
116.27	15552	5.4218	−0.02116
117.95	16986	5.3654	−0.02101
120.14	18981	5.2894	−0.02082
121.57	20385	5.2428	−0.02070
123.14	22003	5.1907	−0.02057
124.50	23493	5.1480	−0.02046
125.53	24584	5.1058	−0.02038

Table II. Average Deviations Resulting from a Comparison Between Experimental and Calculated Vapor Pressures Using Equation 7

	No. of Points	Av. Dev., %
Baly (*1*)	27	1.07
Cath (*4*)	9	0.28
Crommelin (*5*)	11	1.29
Dodge and Davis (*7*)	29	0.67
Fischer and Alt (*8*)	19	2.04
Friedman and White (*9*)	18	0.36
Giauque and Clayton (*11*)	10	0.13
Henning (*12*)	14	0.62
Holst and Hamburger (*13*)	3	1.07
Keesom and Bijl (*15*)	19	0.13
Olzewski (*17*)	3	1.04
Porter and Perry (*18*)	11	1.14
von Siemens (*21*)	7	0.72
Wroblewski (*24*)	3	116

Table III. Vapor Pressures of Liquid Nitrogen Calculated with Equation 7

	T, ° K.	P, Mm.
Triple point	63.14	93.97
	65.0	130.9
	70.0	189.8
	75.0	571.5
Normal boiling point	77.34	760.0
	80.0	1,028
	85.0	1,718
	90.0	2,703
	92.5	3,328
	95.0	4,051
	97.5	4,882
	100.0	5,830
	102.5	6,904
	105.0	8,112
	107.5	9,465
	110.0	10,974
	112.5	12,648
	115.0	14,498
	117.5	16,539
	120.0	18,782
	122.0	20,732
	124.0	22,831
	125.0	23,938
	126.0	25,087
Critical point	126.15	25,263

and Holst (*14*) and White, Friedman, and Johnston (*23*), $P_c = 33.52$ atm. This difference of $33.52 - 33.24 = 0.28$ atm., amounts to 4.1 p.s.i. at the critical point and therefore Equation 7 is applicable with a good degree of precision in the vicinity of the critical point.

NOMENCLATURE

a = van der Waals' constant, (cc./gram mole)^2 atm.
A, B, C, D = constants for Equation 1
d_c = critical density, grams/cc.
P = vapor pressure, mm. of Hg
P_1 = vapor pressure of reference point, mm. of Hg
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
P_t = triple point pressure, mm. of Hg
R = gas constant, 82.055 atm. cc./gram mole ° K.
t_c = critical temperature, ° C.
T = temperature, ° K.
T_1 = temperature of reference point, ° K.
T_b = normal boiling point, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
T_t = triple point temperature, ° K.
v_c = critical volume, cc./gram mole
X = temperature modulus, $(1/T - 1/T_1)/\log T/T_1$
Y = vapor pressure modulus, $\{\log P/P_1 - D(P/T^2 - P_1/T_1^2)\}/\log T/T_1$
z_C = critical compressibility factor, $P_c v_c/RT_c$

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